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Influence of solvent environment on dielectric behaviour of cyclohexylamine

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bstract Dielectric study of cyclohexylamine has been carried out with three non-polar solvent such as benzene, n-heptane and 1,4-dioxane at 3K. Molar polarization (P_2), Kirkwood correlation factor (g), excess correlation factor (δg) and excess free energy (ΔG) have been determined for molecule as a function of mole fraction of solute using static dielectric constant and dielectric constant at optical frequency. The g values are greatly lected by the presence of different environment. In 1,4-dioxane, the high values of g as compared to other two environments is explained on the basis hydrogen bonding interaction. Presence of α and β multimers is identified for all the three environments.

eywords Dielectric constant, Kirkwood correlation factor, molar polarization

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. Introduction

yclohexylamine (CHA) is of prime industrial significance and onstitute some most important insecticides, plasticizers and orrosion inhibitors. The molecules of this compound have everal hydrogen bonding sites and can enter into intermolecular ydrogen bonding giving rise to several different multimers. There is a great interest to study the dielectric behaviour of HA with non-polar solvents to understand the role of hydrogen onding and the effect of solvent environment regarding their iquid structure.

To understand the dielectric behaviour of the associating molecule it is necessary to determine various dielectric parameter ie molar polarization, Kirkwood correlation factor, excess correlation factor and excess free energy *etc*. Those are related with inter or intramolecular association. These parameters have been used to throw light on the dynamic characteristics of molecular association in the binary mixtures of polar and non-polar liquids. In the recent past, few workers [1-4] have studied the dielectric properties of amines in non-polar solvents.

The objective of the paper is to study the dielectric relaxation of CHA in different non-polar environment such as benzene, n-heptane and 1,4-dioxane over the entire range of concentration at temperature 313K. The molar polarization, Kirkwood correlation factor, excess correlation factor and excess free energy have also been calculated in the present study.

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2. Method of measurement and analysis of data

Static permittivity (ϵ_0) at 100 kHz was measured using a dipole meter by directly measuring the capacitance and calibrating it for standard liquids. The dielectric constant (ϵ_∞) at optical frequency was obtained by squaring the refractive index for sodium D-lines, measured with the help of an Abbe's refractometer. The accuracy of measurements of ϵ_0 and ϵ_∞ are nearly 0.1% and 0.03% respectively. The density measurement was made with a pycknometer. All measurements were made at constant temperature 313K.

Kirkwood correlation factor g has been calculated using the modified Kirkwood-Fröhlich [5] equation for the binary mixture given by

$$g\mu^2 = \frac{9KT(2\epsilon_m + \epsilon_\infty)^2}{4\pi N f_2 (\epsilon_\infty + 2)^2 (2\epsilon_m + 1)} V(\epsilon_m - 1) - \frac{3V_1 f_1(\epsilon_1 - 1)}{2\epsilon_m + \epsilon_1} - \frac{3V_2 f_2(\epsilon_\infty - 1)}{2\epsilon_m + \epsilon_\infty} \quad (1)$$

Here, ϵ_m is the static dielectric constant of the solution, ϵ_∞ is the square of refractive index at the frequency of D-lines of sodium for pure solute, ϵ_1 is the static dielectric constant of pure solvent, f_1 is the mole fraction of the solvent, f_2 is the mole fraction of the solute, V is the molar volume of the solution and V_1 and V_2 are the molar volume of pure solvent and pure solute respectively. K, T and N are Boltzmann's constant, absolute temperature and Avogadro's number, respectively. Molar polarization [3] of binary mixture is given by

$$P = \left(\frac{\epsilon_m - 1}{\epsilon_m + 2}\right)V = \frac{\epsilon_m}{\epsilon_m + 2}\left[\frac{3V_1 f_1(\epsilon_1 - 1)}{2\epsilon_m + \epsilon_1} + \frac{3V_2 f_2(\epsilon_\infty - 1)}{2\epsilon_m + \epsilon_\infty} + g\frac{4\pi N\mu^2 f_2(\epsilon_\infty + 2)^2(2\epsilon_m + 1)}{9KT(2\epsilon_m + \epsilon_\infty)^2}\right]. \quad (2)$$

Molar polarization P_2 of the solute is calculated by the equation

$$P_2 = P_1 + \left\{\frac{(P - P_2)}{f_2}\right\}, \quad (3)$$

where P_1 is the molar polarization of the solvent which is given by

$$P_1 = \left\{\frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)}\right\}V_1. \quad (4)$$

The excess Gibb's free energy of mixing (ΔG_I) in the binary mixture was obtained by the expression used by Swain and Roy [6]. David and Douheret [7] developed a mixture equation purely from empirical considerations and introduced a parameter called excess correlation factor (δg) to represent the departure from ideality. Ray and Roy [8] also give the expression for excess free energy of mixing (ΔG_{II}) for the binary mixture of polar and non-polar solvents using excess correlation factor δg in place of g.

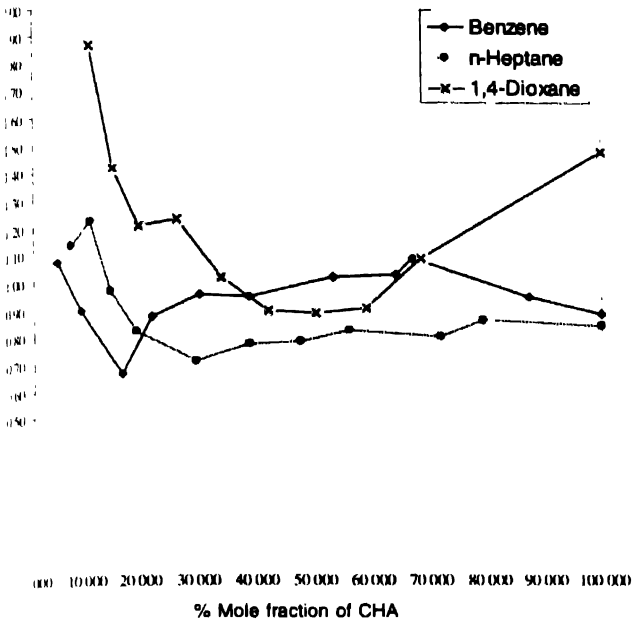
3. Results and discussion

The dielectric constant of CHA in three non-polar solvents, *viz.* benzene, n-heptane and 1,4-dioxane were measured at 313K. Experimental data are listed in Table 1. The variation of g values for CHA against percentage mole fraction ($\%f_2$) are shown in Figure 1. It is clear from the graph that g values are greater than and less than unity, which shows that these molecules associate to form multimers with parallel dipole moment and also with anti parallel dipole moment. The value of $g > 1$ indicate predominance of α - multimers with parallel dipolar orientation, whereas $g < 1$ indicates the predominance of β - multimers with anti-parallel orientation. The observed values of g for benzene with concentration varies monotonously leading to the conclusion that there is no regular ordering of molecular association with the variation of concentration. Similar trends in g values for glycols in benzene were obtained by Sengwa and Kaur [9]. In n-heptane, as the dilution decreases, g values decreased to unity which shows that a-multimers are converted in β - multimers. As the mole fraction of CHA increases, g values are less than unity indicating that the molecules of these compound associate

Table 1. Values of ϵ_0, g, P_2, δg, ΔG_I and ΔG_{II} with concentration in different solvents at 313K.

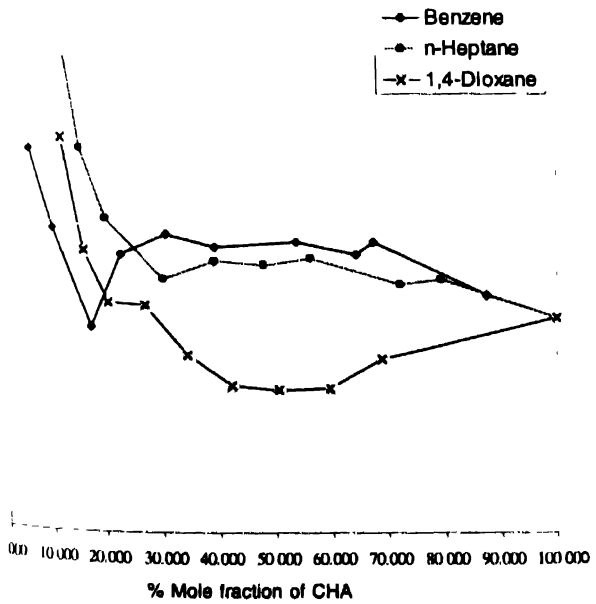
Mole fraction of CHA	ϵ_0	g	P_2 (cc)	δg	ΔG_I (J/mole)	ΔG_{II} (J/mole)
			Benzene			
0.05075	2 444	1 07	85 86	0.19	29 14	28 13
0 09627	2.544	0.89	76 27	-0.04	51.22	46 67
0 17140	2.600	0 66	64.46	-0.32	86.76	68 61
0.22435	2.872	0 86	73.27	-0 11	91 33	71 35
0.30591	3.192	0.94	75.70	-0.02	96.63	69 26
0 39126	3 440	0.93	74 18	-0.1	98 27	62 41
0 53638	4.016	1 00	74.78	+0 08	69 59	37 89
0 64282	4.336	1 01	73 19	0.09	47.99	21 76
0 67286	4 592	1.07	74.69	0 16	24 42	11 66
0 87409	4 760	0.93	68 39	0 04	11 17	2 07
1 0	4 86	0.87	65 73	0 58	0	0
			Heptane			
0 07752	2.064	1 13	101 47	0 06	71 42	56 57
0 11368	2 164	1 21	99.89	-0.04	104 52	73 73
0 15033	2 192	0 96	86.04	-0 36	144 34	86 22
0 19686	2 242	0 81	77 54	-0 15	135 79	106 58
0 30019	2.392	0.70	70 26	-0.25	179 11	117 83
0 39152	2.648	0 76	72.37	-0.18	191 73	110 72
0 47892	2.888	0 77	71 98	-0 15	193 26	84 61
0 56272	3 192	0 81	72 70	-0 09	175 57	74 85
0 72018	3.672	0 79	69.58	-0.08	139 54	35 27
0.79426	4.080	0.85	70.26	-0.01	91 69	20 79
1.0	4 86	0 83	65 73	-0.04	0	0
			1,4-Dioxane			
0.11365	2.62	1.85	87.25	0.80	36 51	33 96
0 15642	2.630	1 40	73.64	0.33	50 88	42 53
0 20242	2 670	1.19	67.40	0.10	65 21	48 89
0 26765	2.834	1 21	67 20	0.09	78 47	52 91
0 34301	2.856	1.00	61 13	-0.15	101 91	53 35
0.42228	2 892	0.88	57.48	-0.31	125 87	47 20
0.50576	3.016	0.87	57.00	-0.35	141.30	36 30
0 59380	3.168	0.89	57.07	-0.37	151 50	21 87
0.68679	3.560	1 07	60 76	-0.24	127 30	14 43
1 0	4.86	1.45	65.73	-2.05×10^{-4}	0	0

orm multimers with anti-parallel dipole moment. In 1,4 dioxane, are getting the presence of α and multimers β also.



gure 1. Variation of g with % mole fraction of CHA.

Among the system studied above, the deviation of g from nity for 1,4-dioxane is higher than those of n-heptane and enzene This may be attributed to the fact that CHA establishes bonding with oxygen of 1,4-dioxane and results in enforcement of intermolecular association of CHA molecule nd hence increases the value of g. Similar results were obtained y Acharya *et al* [10] in the case of dioxane for di-isobutyl etone (DBK): Molar polarization P_2 (CC) of CHA with three on-polar solvent shows anomalous behaviour with mole raction of CHA [Figure 2] *i.e.* there are increase as well as



2. Variation of P_2 with % mole fraction of CHA.

decrease in P_2 values with increasing concentration of CHA. It is clear from Figures 1 and 2 that molar polarization P_2 follows the Kirkwood correlation factor g with the variation of concentration. At higher values of g, molar polarization is large while for lower g values, it is small. These maxima and minima in P_2 values are found at the same concentration where these have been observed in g values. This shows that the association in these molecules is quasi-state *i.e.* there is continuous rapid switching of the dipole from intramolecular state to intermolecular and *vice versa.*

The excess free energy (ΔG_{II}) are plotted with percentage mole fraction of CHA [Figure 3]. It is clear from the graph that ΔG_{II} values are positive for all the mixtures. The magnitude of $(\Delta G)_{max}$ for n-heptane mixture being highest, corroborates our findings on g and P_2 that the extent of formation of β clusters is maximum in this system. The value of ΔG_{II} is observed to be minimum in 1,4-dioxane in comparison to benzene and n-heptane. This supports our earlier finding that the interaction in 1,4-dioxane medium is stronger than that of other two medium. Since the nature of the non-polar liquids in our present study is non-associative in the mixture, the negative values of δg and the positive nature of ΔG_{II} confirm the mathematical formulation used by Ray and Roy [8]. With increase in the concentration of CHA (polar liquid), ΔG_{II} increases and attain the maximum value in the range 0.23-0.34 mole fraction of CHA and then decreases. This may be due to the fact that β - multimers in the mixture is characterized by reduction of internal energy in comparison to α - multimers in CHA. With further increase in the concentration of CHA, the conversion of β - multimers to α - multimers reverses the trend and ΔG_{II} starts diminishing.

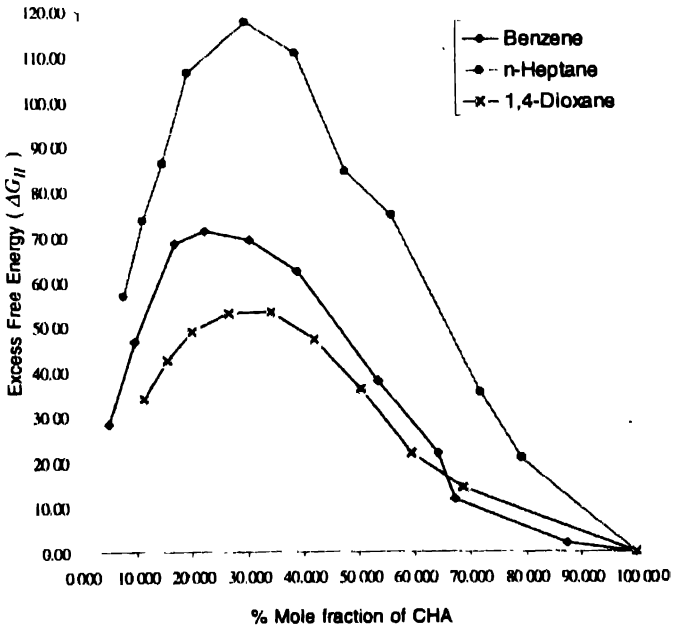


Figure 3. Variation of ΔG_{II} with % mole fraction of CHA.

4. Conclusion

We may thus conclude as follows :

(i) The presence of α - and β - multimers exist in all the three environments under investigation.

(ii) CHA establishes H- bonding with oxygen of 1,4-dioxane causing reinforcement of inter molecular association of CHA molecule. This effect shows deviation of g from unity which is much higher in 1,4-dioxane as compared to n-heptane and benzene.

(iii) Study of molar polarization shows continuous rapid switching of dipole from intramolecular to intermolecular state and vice-versa.

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